

## On charge and orbital ordering in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$

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**Abstract.** Using first principle band structure calculations, we critically examine results of resonant x-ray scattering experiments which is believed to directly probe charge and orbital ordering. Considering the specific case of  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ , we show that this technique actually probes most directly and sensitively small structural distortions in the system. Such distortions, often difficult to detect with more conventional techniques, invariably accompany and usually cause the orbital and charge orderings. In this sense, this technique is only an indirect probe of such types of ordering. Our results also provide a microscopic explanation of the novel types of charge and orbital ordering realized in this system and other doped manganites.

In recent times the doped manganites have revealed a wide range of physical properties resulting from a strong interplay between the spin, charge and lattice degrees of freedom [1]. In some of the hole-doped systems, the charge carriers preferentially occupy certain orbitals, known as orbital ordering (OO) or sometimes certain atomic sites, resulting in charge ordering (CO). The microscopic origin of these phenomena, especially the charge ordering have been explained invoking long-ranged Coulomb interactions [2]. It is also possible that such orbital and charge orderings are driven by, or at least, substantially assisted by lattice distortions, not considered in a purely electronic mechanism.

It has been suggested [3, 4, 5] that resonant x-ray scattering can directly probe the orbital and charge orderings. To describe the technique briefly, X-ray diffraction experiments are carried out using photon energies in the vicinity of an absorption edge to fulfil the resonant condition and the intensities of the diffraction spots are monitored as a function of the photon energy. While the intensities corresponding to the superlattice spots arising from charge or orbital orderings are generally very weak, these exhibit remarkable enhancement at the absorption threshold, enabling one to detect them easily. This sensitivity in the diffraction intensity from the superlattice spots arises from the fact that the X-ray scattering tensor is sensitive to various anisotropies such as orbital ordering and charge ordering. If a superlattice reflection is identified as arising due to a certain orbital ordering occurring at atomic sites A and B, with the energy splitting between the two specific orbitals involved in the ordering equal to  $\Delta$ , it has been shown [4] that the intensity of the superlattice reflection at resonant conditions is proportional to  $\Delta^2$ . Similarly at a charge ordering superlattice reflection, the same dependence on  $\Delta$  is seen. This technique has been extensively used to probe orbital and charge ordering [3, 4, 5] in  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{LaSr}_2\text{Mn}_2\text{O}_7$ ,  $\text{NaV}_2\text{O}_5$ ,  $\text{LaMnO}_3$  and  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ .

In order to understand the microscopic origin of such orderings, we have studied a system,  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ , in which both orbital as well as charge orderings are present. Mn in this system has an average valence of 3.5. X-ray resonant scattering experiments [5] have been interpreted to establish that one of the Mn sites has a valence of 3+, while the other Mn site has a valence of 4+, giving rise to an integral valence fluctuation between the two Mn sites arranged alternately in the lattice. This system appears to be an ideal testing ground, since preliminary crystal structure data [6] did not provide any evidence for any significant lattice distortion, suggesting a purely electronic origin for the charge and orbital orderings. Of course, a purely electronic mechanism, *via* electron-electron interactions, will be inaccessible to single-particle theories; however, as we shall show, first principle band structure results strongly suggest [7] an alternate origin of the observed phenomena, while simultaneously establishing significant lattice distortions in this system.

We have used the plane-wave pseudopotential method to calculate the electronic structure of  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ . Ultrasoft pseudopotentials were used for Mn and the La/Sr site. We used virtual crystal approximation in order to treat alloying effects of La and Sr. The generalised gradient approximation [8] was used for the exchange functional, and the calculations were performed over a k-grid of  $4 \times 4 \times 2$ . The lattice parameters of the unit cell were kept fixed at the experimentally deduced values, and the internal positions were optimised.

Neutron diffraction experiments [9] establish that the Mn spins order below 110 K forming one-dimensional zig-zag ferromagnetic chains in the *ab*-plane, coupled antiferromagnetically to each other (see Fig. 1(a)). The high temperature structure of the compound is found to be Immm, with the Mn-O bondlengths equal to 3.66 a.u in the *ab*-plane, while the Mn-O bondlength of the apical oxygens was found to be 3.74 a.u. At 217 K, a charge and orbital ordering transition is found to take place, and the Mn sites form a pattern of alternating "Mn<sup>3+</sup>-Mn<sup>4+</sup>" sites in the *ab*-plane. A symmetry lowering was believed to take place, and the experimental data [9] were interpreted as arising from a breathing-mode like movement of the oxygen atoms in the *ab* plane towards one set of Mn atoms, identified as the higher valent "Mn<sup>4+</sup>" sites. As the structural information of this compound is shrouded in controversy, we optimised the internal positions. This proposed structure is found to have a higher energy in our calculations.

The exchange splitting at the Mn site is  $\sim 3$  eV. Consequently the hopping amplitude between adjacent zig-zag chains of Mn atoms which are coupled antiferromagnetically is small. Hence the electronic structure is governed by these one-dimensional chains. Considering a single chain as shown in Fig. 1(a), it was shown [10] that the anisotropic hopping between the Mn *d* orbitals could explain the OO at the two Mn sites. We have performed *ab-initio* calculations considering the complete 3-dimensional Immm structure [6]. Similar to the findings in ref. [10], we also found the kind of OO that is observed experimentally. While the  $d_{3x^2-r^2}$  orbital was preferentially occupied on Mn(1) atom, the  $d_{3y^2-r^2}$  orbital was preferentially occupied on the other Mn(3) atom (see Fig. 1a). These results can be understood within the framework of a simple nearest neighbour tight-binding model involving the  $e_g$  orbitals shown in Fig. 1(a):  $d_{3x^2-r^2}$  and  $d_{y^2-z^2}$  on Mn(1),  $d_{3y^2-r^2}$  and  $d_{z^2-x^2}$  on Mn(3) as well as  $d_{3z^2-r^2}$  and  $d_{x^2-y^2}$  on Mn(2) and Mn(4) as used in Ref. [10]. While the  $d_{3x^2-r^2}$  orbital at Mn(1) and  $d_{3y^2-r^2}$  orbital on Mn(3) hybridize with both  $e_g$  orbitals on Mn(2) and Mn(4), the  $d_{y^2-z^2}$  on Mn(1) and  $d_{z^2-x^2}$  on Mn(3) do not. The eigenvalue spectrum of such a simple model, consists of two bonding bands, energetically separated from four non-bonding bands, with

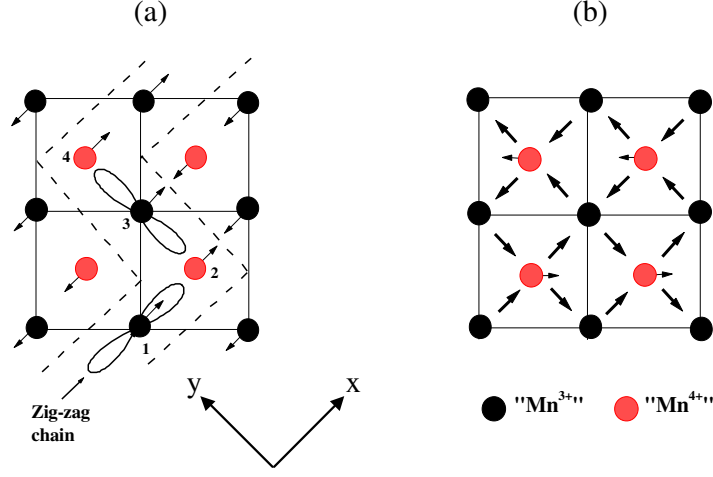


Figure 1: (a) A schematic figure of the spin, charge and orbital ordering of Mn atoms in the *ab* plane. The magnetic structure consists of zig-zag chains of ferromagnetic Mn atoms coupled antiferromagnetically to neighboring chain atoms. Dashed lines are drawn parallel to the zigzag chains to highlight each chain. (b) The direction of displacement of the oxygen atoms are indicated with thick arrows, while small arrows show the direction of displacement of the Mn atoms. The choice of *x* and *y* axes used in the paper is also shown.

the antibonding bands at higher energies. As the average valence of Mn is 3.5, there are two electrons in the  $e_g$  orbitals of the 4 Mn atoms comprising the chain. Hence the two bonding bands which have dominantly  $d_{3x^2-r^2}$  character on Mn(1) and  $d_{3y^2-r^2}$  character on Mn(3) are occupied. Thus, the one-dimensional chains which are a consequence of the magnetic structure drive the OO within these calculations. However, the difficulty in approaching the problem this way is that the Immm structure exists only above the CO/OO temperature and there are extensive evidence in the literature suggesting a symmetry lowering below the ordering transition. However, the exact details of the experimental crystal structure of this compound is not available, specifically there is no information on the atom positions. It was suggested [9] that the structure, within the charge ordered state, is Cmmm with lattice constants equal to  $\sqrt{2}a$ ,  $\sqrt{2}a$ , *c* where *a* and *c* are the cell dimensions of the basic Immm cell. More recent work by Larochelle *et al.* [11], however, indicate that the structure is Ammm or one of its two subgroups Am2m or A222, with the lattice parameters being  $\sqrt{2}a$ ,  $2\sqrt{2}a$ , and *c*. None of the structural investigations have been able to provide the atom positions, particularly for the oxygen sites, owing to the large unit cell and the existing data quality [11]. Ref. [11], however, suggests certain possible distortions of the oxygens, though not in agreement with ref. [9]. The structure we find is Bmmm with lattice parameters  $\sqrt{2}a$ ,  $2\sqrt{2}a$  and *c*. The lattice parameters that we have obtained are in agreement with those of

ref. [11, 12].

On optimizing the internal coordinates, the system exhibited different distortions of the  $\text{MnO}_6$  octahedra associated with different Mn atoms. The direction of displacement of the oxygen atoms in the *ab*-plane is indicated by the arrows shown in Fig. 1(b), though the oxygen atoms have been left out of the figure for added clarity. The Mn site, Mn(3), showing  $d_{3y^2-r^2}$  OO lowered its energy by an elongation of the Mn-O bonds in the *y*-direction. This kind of distortion can be understood easily within the framework of crystal-field effects. A tetragonal distortion of a  $\text{MnO}_6$  octahedron resulting in an elongation of the Mn-O bondlengths in the *y*-direction, lowers the bare energy of the  $d_{3y^2-r^2}$  orbital. Thus, the sites Mn(1) and Mn(3) behave like a "Mn<sup>3+</sup>" species, sustaining a Jahn-Teller (JT) like distortion of the surrounding oxygens in two mutually perpendicular directions, giving rise to the orbital ordering. As a consequence, the oxygen atoms surrounding the sites labelled Mn(2) and Mn(4) sustain distortions with the oxygen atoms along the *x*-axis being displaced in one direction and the ones along the *y*-axis being displaced in another direction, as shown in the figure, in contrast to the suggestion in ref. [9] where all four oxygen atoms surrounding the Mn(2) and Mn(4) sites move closer to the Mn atom. The sites Mn(2) and Mn(4) have been identified as "Mn<sup>4+</sup>" sites in the literature; within our calculations the charge difference between the so-called "Mn<sup>3+</sup>" and "Mn<sup>4+</sup>" species is negligible, suggesting "charge" ordering to be a misnomer in these cases.

While our calculations suggest different distortions of the surrounding oxygens about the "Mn<sup>3+</sup>" and "Mn<sup>4+</sup>" sites, the actual magnitude of the distortion is fairly small [13]. The underestimation of the magnitude of the JT distortion by these first-principles approaches is well-known, though these methods do get the nature of distortions correctly. An example of this is  $\text{LaMnO}_3$  where the nature of distortion was correctly predicted, while the magnitude of the theoretical JT distortion was found to be half of the experimental value [14]. We simulated the neutron diffraction pattern using the optimized coordinates as well as the coordinates assuming a Jahn-Teller distortion equal to what is found in  $\text{LaMnO}_3$ . The simulated diffraction patterns were nearly identical, indicating the difficulty of determining the oxygen positions with any precision from such measurements. It is also significant that with optimized JT distortion, the correct ground state magnetic order cannot be reproduced for  $\text{LaMnO}_3$  [14]. The situation seems to be the same in the present case, where the CE type antiferromagnetic state is more stable than the ferromagnetic state only with the enhanced JT distortion. Hence in the subsequent analysis, we have extrapolated the magnitude of the JT distortion to the value observed in  $\text{LaMnO}_3$ .

The experiments by Murakami *et al.* [5] analyzed the energy dependence of the OO superlattice reflection across the Mn *K* absorption edge. The strong energy dependence was interpreted as arising from a splitting of  $\sim 5$  eV between the  $4p_x$  and  $4p_y$  PDOS at the sites Mn(1) and Mn(3) which show OO. While the  $4p_x$  states were suggested to be 5 eV lower than the  $4p_y$  on one Mn atom, the order was reversed on the other Mn atom. Theoretically there are two contrasting interpretations possible for such a splitting. Ishihara and Maekawa [15] argued in the context of  $\text{LaMnO}_3$  that the splitting in the Mn  $4p$  states induced by the intraatomic  $p-d$  Coulomb interaction produces such a strong tensor character of the scattering form factor. However, it was pointed out [16] that as the  $4p$  states are extended, the suggested  $p-d$  Coulomb interaction strength is unphysically large and the splitting in the  $4p$  states is actually caused by the JT distortion, though Coulomb interactions, particularly

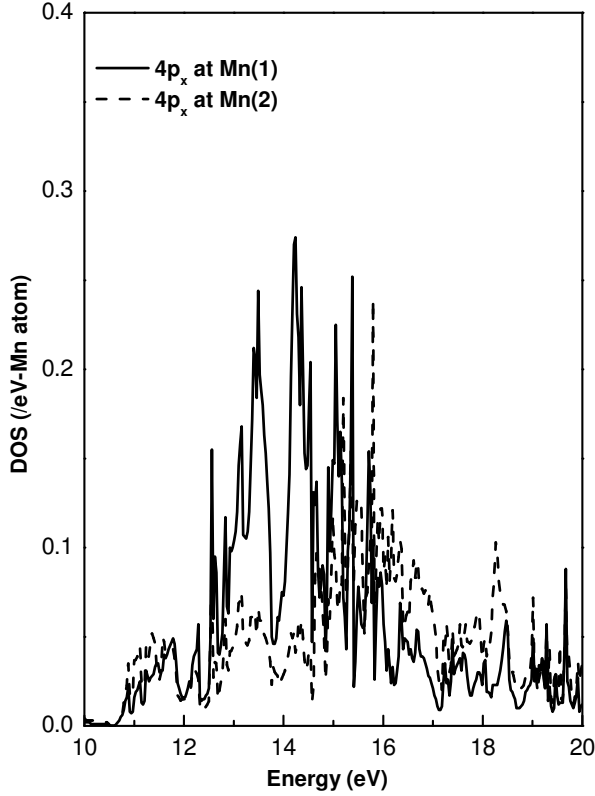


Figure 2: The Mn  $4p_x$  PDOS projected on the sites Mn(1) and Mn(2).

within the Mn  $3d$  manifold, have important consequences for other properties, such as the magnetism, in these systems. These suggestions are consistent with an earlier analysis of transition metal  $K$ -edge XAS in Fe and Co oxides [17]. A splitting of  $\sim 3$  eV is clearly visible in the Mn  $4p$  PDOS at Mn(1), with the  $4p_x$  states located at lower energies. The order is reversed at the other Mn site (Mn(3)) which shows  $d_{3y^2-r^2}$  ordering. Thus, our results on  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$  are consistent with the suggestion [16] in the context of  $\text{LaMnO}_3$  that the JT distortion to be not only the driving force for the orbital ordering, but also responsible for the specific experimental effect of the pronounced tensor character of the form factor *via* the splitting of the  $4p$  partial DOS.

Strong enhancement in the intensity at the energy corresponding to the Mn  $K$ -absorption edge has been observed at the CO superlattice reflection. [5] The experimental results suggest the presence of two types of Mn atoms in the system, with a shift of about 4 eV between the corresponding absorption edges. As the absorption edges of formal " $\text{Mn}^{4+}$ " compounds appear  $\sim 4$  eV above the absorption edge of formal " $\text{Mn}^{3+}$ " compounds, the authors claimed that this was a direct evidence of an ordering of the two distinct charge species - " $\text{Mn}^{3+}$ " and " $\text{Mn}^{4+}$ " in this system. From the present calculations, we find that as the environment for the Mn(1) and Mn(3) sites is different from the environment for the Mn(2) and Mn(4) sites, there is a substantial modification in the Mn  $4p$  PDOS, explaining the shift in the absorption edges, though the net charges associated with these two sites, 4.53 at Mn(1) and Mn(3), and 4.51 at Mn(2) and Mn(4), are almost identical. As shown in Fig. 2 the  $4p_x$

states at Mn(1) are found to lie at lower energies compared to the Mn  $4p_x$  states at Mn(2). Although there is no substantial charge difference, the difference in the magnetic moment between the "Mn<sup>3+</sup>" and the "Mn<sup>4+</sup>" sites is  $0.25 \mu_B$  evaluated within a muffin-tin radius of 2 a.u about each Mn atom. A similar, but more pronounced, effect has been recently found in the case of CaFeO<sub>3</sub>, which was believed to be in a charge disproportionated state of Fe<sup>3+</sup> and Fe<sup>5+</sup> earlier; it has been found [18] that while the charge state at the two Fe sites are very similar, there is a strong lattice distortion that distinguishes these two sites and also stabilises considerably different magnetic moments at the two Fe sites.

In conclusion, we have carried out an analysis of the experimental observations for orbital and charge ordering in La<sub>0.5</sub>Sr<sub>1.5</sub>MnO<sub>4</sub>. Our results indicate the presence of two Mn species with very different environments. One of the Mn species has a JT distortion of the oxygen atoms surrounding that atom and hence, in this sense, may be thought to be similar to an "Mn<sup>3+</sup>" species. The distortions around the other, so-called "Mn<sup>4+</sup>", atoms are different from the simple breathing mode distortion suggested earlier. These results establish that the remarkable sensitivity of the experimental technique to lattice distortions about the absorbing atom *via* the pronounced shift of the unoccupied extended states with such distortions, can provide valuable information which traditional techniques such as neutron scattering may not be able to provide. This is evident from Fig. 2. However, it is inappropriate to claim that this technique provides a *direct* probe to the charge and orbital orderings.

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